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METHOD FOR MAKING PHENOL, ACETONE AND METHYL ETHYL KETONE

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[There are no amendments to this patent.]

Claim

Method for making phenol, acetone, and methyl ethyl ketone, characterized by involving a process for forming sec-butylbenzene hydroperoxide by liquid phase reaction of sec-butylbenzene by molecular oxygen-containing gas in the presence of cumene or cumene hydroperoxide; a process of concentrating the reaction product solution of mainly sec-butylbenzene hydroperoxide and cumene hydroperoxide; then a process of subjecting the concentrated solution to a decomposition reaction in the presence of an acidic catalyst for converting the above sec-butylbenzene hydroperoxide and cumene hydroperoxide into phenol, acetone, and methyl ethyl ketone.

Detailed explanation of the invention

Industrial application field

The present invention concerns a novel useful method for the manufacture of phenol, acetone and methyl ethyl ketone, more specifically concerns method for the manufacture of phenol, acetone, and methyl ethyl ketone by liquid phase oxidation of sec-butylbenzene in the presence of cumene or cumene hydroperoxide by co-oxidation of sec-butylbenzene and cumene the decomposition.

The phenol is used as raw material for phenolic resins or various phenol derivatives for basic products of chemical industries. On the other hand, acetone and methyl ethyl ketone are used as solvents, methyl ethyl ketone is especially used for coating solvents.

Prior art and problems to be solved by the invention

According to prior art, sec-butylbenzene is oxidized to obtain sec-butylbenzene hydroperoxide (hereafter referred to S-HPO), then this S-HPO is subjected to a decomposition reaction in the presence of an acidic catalyst to obtain phenol and methyl ethyl ketone as disclosed in the literature (Japanese Kokai Patent Application Nos. Sho 48[1973]-80524 and Sho 51[1976]-133239; JCS, 2076-2077 (1949)).

In making phenol and methyl ethyl ketone from sec-butylbenzene as shown above, two processes are involved, i.e., first a process of oxidation of sec-butylbenzene to S-HPO, then a process of breaking down the S-HPO in the presence of an acidic catalysts to obtain the two target compounds.

However, the first step of the oxidation reaction is slow, thus highly concentrated S-HPO cannot be obtained in a short period of time, and a drawback is the formation of the byproduct acetophenone in large quantities.

The i-butylbenzene present in a minute amount in the sec-butylbenzene is quite poisonous to the oxidation reaction rate.

Yet, the sec-butylbenzene and i-butylbenzene have essentially the same boiling point, thus their separation is difficult, and the formation of a small amount of i-butylbenzene in the sec-butylbenzene preparation cannot be avoided.

Considering the difficulties in the prior art, we have attempted the following:

① The sec-butylbenzene oxidation rate is increased by performing the oxidation in the presence of cumene, which has a high oxidation rate, to accelerate the oxidation of sec-butylbenzene to be the same as cumene.

② Breaking the dependence of the S-HPO formation rate on the i-butylbenzene content in sec-butylbenzene. This also done by co-oxidation of sec-butylbenzene and cumene.

③ Reduction of the byproduct acetophenone formation. Presence of cumene was effective.

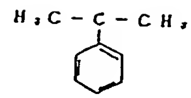
Means to solve the problems

Next, we further developed the above facts and discovered that when S-HPO is formed by liquid phase oxidation of sec-butylbenzene by molecular oxygen-containing gas in the presence of cumene or cumene hydroperoxide, the sec-butylbenzene oxidation rate is high with a reduced formation of the byproduct acetophenone, while the oxidation rate is not affected by the i-butylbenzene content in the raw material sec-butylbenzene. Thus, the present invention is attained.

Namely, the present invention provides a method for producing phenol, acetone and methyl ethyl ketone, characterized by involving a process for forming S-HPO by a liquid phase reaction of sec-butylbenzene by molecular oxygen-containing gas in the presence of cumene or cumene hydroperoxide; a process of concentrating the reaction product solution of mainly S-HPO and cumene hydroperoxide; then a process of subjecting the concentrated solution to a decomposition reaction in the presence of an acidic catalyst for converting the above S-HPO and cumene hydroperoxide into phenol, acetone, and methyl ethyl ketone.

First, the oxidation of cumene and sec-butylbenzene proceeds as shown below:

Provided that



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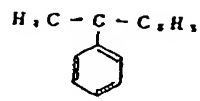


is R,

$$RH + ROO\cdot \longrightarrow R\cdot + ROOH \qquad (I)$$
$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (II)$$

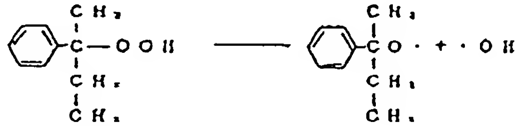
At this time, the ROOH formed in the equation (I) undergoes the following decomposition as side reaction:

$$ROOH \longrightarrow RO\cdot + \cdot OH \qquad (III)$$

Now, provided cumene hydroperoxide is C-HPO, this is due to the higher C-HPO formation rate than S-HPO.

Also, the big difference between S-HPO and C-HPO is in the fact that the thermal stability of the byproduct formed by the equation (III) is entirely different.

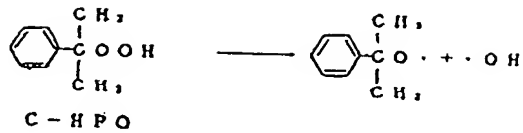
Namely,



(IV)

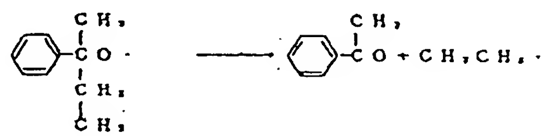
S-HPO

β-methylcumyloxy radical

 (V)

cumyloxy radical

The β-methylcumyloxy radical is very unstable and undergoes the following decomposition to acetophenone

 (VI)

On the other hand, cumyloxy radical is stable, and provided this radical is RO•, following reaction proceeds:

$$RH + RO\cdot \longrightarrow R\cdot + ROH \qquad (VII)$$

The rate-determining step of the oxidation reaction seems to be the hydrogen abstration from RH as shown in the equation (I).

It can postulated that if the hydrogen abstraction reaction of RH, i.e., sec-butylbenzene, is performed at the stable C-HPO decomposition product, not at the unstable S-HPO decomposition product, S-HPO formation rate becomes high.

As a result of a further study taking this point into account, we have discovered that in the "cumene method," when the sec-butylbenzene oxidation is carried out in the presence of C-HPO concentrate as a reaction aid or the sec-butylbenzene oxidation is carried out in the presence of cumene which becomes C-HPO when oxidized, the S-HPO yield can be increased, and in the process, the oxidation rate is high with reduced byproduct acetophenone formation with no effect

of i-butylbenzene that is present as a minute impurity in the raw material sec-butylbenzene, resulting in a reaction process with a very high oxidation rate.

In addition, when no separation of S-HPO and C-HPO occurs, the oxidation reaction solution (concentrate) obtained is subjected to decomposition reaction in the presence of an acidic catalyst, the desired phenol, acetone, and methyl ethyl ketone can be obtained.

Next, the method of the present invention is explained in further detail. It is desirable that the oxidation reaction is carried out using a molecular oxygen-containing gas under pressure above the ambient pressure. The higher the pressure, the faster the acceleration of the oxidation reaction, while the pressure is preferably 1-20 kg/cm^2.

At a lower reaction temperature, the selectivity for S-HPO is higher, but the reaction rate decreases. On the other hand, as the reaction temperature increases, the decomposition of C-HPO and S-HPO increases, and industrially, the temperature range of 90-145°C is preferred.

The C-HPO concentrate which is a reaction aid in this oxidation reaction is a concentrate of the oxidation reaction product in the conventional cumene method, usually with a C-HPO content about 65-85 wt%. The amount of its addition should be a C-HPO concentration of 5-60 wt%, preferably 5-30 wt% in the oxidation reaction solution (concentrate).

In the case of the co-oxidation of cumene and sec-butylbenzene, the percentage of cumene (between the cumene and sec-butylbenzene) is preferably above 50 wt%, more preferably between 30-70 wt%.

In this case, first cumene is oxidized to C-HPO, then S-HPO is formed.

The reaction time of this oxidation reaction should be 0.5-10 h, preferably 1-3 h.

With an increased reaction percentage, the selectivity for S-HPO decreases, thus in terms of selectivity, a reduced reaction percentage seems to be desirable, but this will result in reduced yield per unit volume of the reactor, thus the reaction percentage 5-20% is preferred.

The molecular oxygen-containing gas may be pure oxygen or oxygen mixed with an inert gas, while air can be used favorably.

After the oxidation reaction, the reaction product solution contains 3-15 wt% S-HPO, 10-65 wt% C-HPO, unreacted starting material, byproducts, etc. By vacuum distillation, the starting material sec-butylbenzene or cumene can be removed from the reaction product solution.

As a result, concentration can be done to 30-70 wt% of the original liquid.

Next, the concentrate is subjected to the decomposition reaction. By this reaction, S-HPO is converted to phenol and methyl ethyl ketone and C-HPO to phenol and acetone.

The decomposition reaction can be carried out in a conventional manner in various organic solvents in the presence of an inorganic acid or acidic material such as hydrogen fluoride, boron fluoride, nitric acid, hydrochloric acid, etc., or ion-exchanged solid catalysts.

After this decomposition reaction, the reaction product solution is separated from the catalyst, freed from low boiling components such as solvent by distillation and distilled to separate phenol and acetone and methyl ethyl ketone to obtain products.

Application examples

Next, the present invention is explained in further detail with application examples. Unless stated otherwise, % is by weight.

Application Example 1

Into a 1-L reactor, air was blown into a mixture of 134 g sec-butylbenzene and 600 g cumene at 120°C and the reaction was performed under a pressure of 5 kg/cm^2G for 4 h.

During the oxidation reaction, 2% sodium hydroxide aqueous solution was added to prevent the reaction system from becoming acidic.

This oxidation reaction yielded 108 g C-HPO and 14.9 g S-HPO.

Gas chromatography showed 91% for selectivity of S-HPO.

Next, the oxidation reaction product solution was concentrated in vacuo at 10 mm Hg to recover sec-butylbenzene and cumene and to obtain 180 g concentrate containing 60% C-HPO and 8.3% S-HPO.

In a 250-mL glass reactor, 100 g acetone and 30 g of the above concentrate were cooled below 50°C, while 0.1 g sulfuric acid was added and heated for 30 min for decomposition of both the hydroperoxides.

As a result, both peroxides of C-HPO and S-HPO were completely decomposed, giving phenol, acetone and methyl ethyl ketone in yields of 95% each.

Application Example 2

Into a 1-L reactor, air was blown to 600 g cumene at 120°C, and the reaction was performed under a pressure of 5 kg/cm^2 for 3 h to obtain 15% C-HPO, which was then concentrated in vacuo at 10 mm Hg to obtain a C-HPO concentrate (C-HPO 72.3%, cumyl alcohol 9.7%, acetophenone 2.0%, cumene 18.0%).

In a 500-mL titanium reactor, 100 g of the above concentrate was treated with 300 g sec-butylbenzene, blown with air and the reaction was performed under a pressure of 5 kg/cm^2 for 4 h at a temperature of 120°C.

The composition analysis of the reaction product solution showed 75.2 g C-HPO and 34.2 g S-HPO. The sec-butylbenzene reaction rate was 10%, and the selectivity for S-HPO 92%.

Next, the oxidation reaction product solution was heated in vacuo at 10 mm Hg until the bottom part reached 50°C to remove the light fractions such as sec-butylbenzene and cumene to obtain 150.5 g concentrate containing 50% C-HPO and 22.7% S-HPO.

Then, a mixture of 100 g acetone and 30 g of this concentrate was cooled with ice.

After addition of 0.1 g hydrochloric acid, the mixture was heated at 50°C for 30 min for decomposition of both peroxides.

Both peroxides of C-HPO and S-HPO were completely decomposed, giving phenol, acetone and methyl ethyl ketone in yields of 94.2% each.

The sec-butylbenzene used in this example contained 1.4% i-butylbenzene.

Comparative Example 1

In a 1-L reactor, 73.4 g sec-butylbenzene were blown with air and the reaction was performed under a pressure of 5 kg/cm^2 for 4 h a temperature of 120°C, with formation of 17.6 g S-HPO and S-HPO concentration of 2.9%.

The reaction further continued for 10 h with the formation of 58.7 g S-HPO and S-HPO concentration of 8.0%.

When the reaction was further continued for 14 h, 11.2% S-HPO was formed, and in terms of reacted sec-butylbenzene, the selectivity for S-HPO was 72%.

The sec-butylbenzene used in this example contained 1.4% i-butylbenzene.

Effects of the invention

(1) By the presence of C-HPO or cumene that forms C-HPO when oxidized, in the sec-butylbenzene oxidation reaction, the S-HPO yield is increased with a reduced formation of byproducts, leading to increased final yields of phenol and methyl ethyl ketone.

(2) The oxidation rate of sec-butylbenzene to S-HPO is high. Even when using sec-butylbenzene containing 1.4% i-butylbenzene, this oxidation rate is high.

(3) The target decomposition products acetone and methyl ethyl ketone can be easily separated by distillation.

(4) Cumene and C-HPO are available inexpensively in direct connection to the means of phenol synthesis by the cumene process.